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# **POTENTIAL AMINOQUINONE INHIBITORS OF CE AND BMI/CARBON FIBER/ALUMINUM COMPOSITE GALVANIC DEGRADATION**

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## **ABSTRACT**

Bismaleimide (BMI) and cyanate ester (CE) resins are susceptible to degradation by hydrolysis. The chemical conditions necessary to effect resin hydrolysis can be generated by galvanic activity induced in resin/carbon fiber/metal composite structures by salt water/air environments. The objective of this study was to identify resin additives that mitigate resin hydrolysis by mediating the production of chemically basic galvanic corrosion byproducts. A number of aminoquinone compounds were both synthesized and procured for testing as potential inhibitors of the galvanic degradation observed in CE and BMI resin/carbon fiber/aluminum composite structures. It was found that compounds that indicated redox activity in non-aqueous cyclic voltammetry testing, and were soluble in the resin matrix, provided levels of resin hydrolysis protection. This was shown in model CE composites with carbon fiber (70% by weight) under accelerated exposure conditions. The use of these inhibitors in certain aircraft composite structures could either alleviate the requirements for extensive structures overdesign or provide additional degradation protection.

**KEY WORDS:** Corrosion Resistance, Cyanate Ester, Bismaleimides

## **1. INTRODUCTION**

Bismaleimides and cyanate esters are used in graphite reinforced composites in advanced jet aircraft. These composites exhibit degradation under conditions simulating use in aircraft on aircraft carriers - when coupled to metals, including aluminum, in the presence of salt water and air. The mechanism of degradation involves:

- oxidation of the metal, forming metal cations and electrons.
- electron conduction through graphite fiber reinforcement.

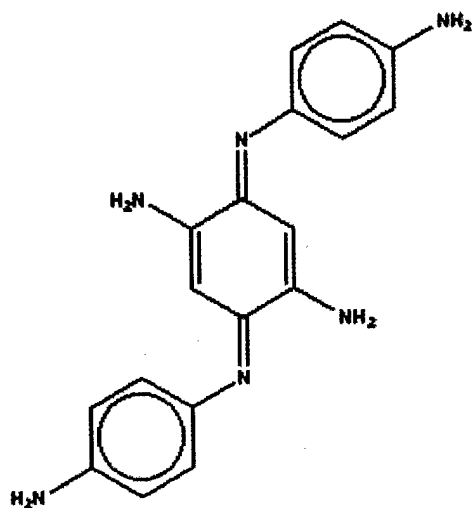
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- reduction of dissolved oxygen in water, forming hydroxide ions.
- and base catalyzed hydrolysis of the polymer linkages.<sup>1-6</sup>

Polyamine quinones have been extensively investigated as metal binding, high temperature resistant redox polymers, as salt water resistant coating materials, and as curing agents to enhance the adhesion of epoxy matrix resins in fiberglass reinforced composites.<sup>7-12</sup>

This research was performed to investigate the use of quinone/amines as electron scavengers to inhibit BMI/CE degradation. Two polyquinoneamines were synthesized, and their reactions with sodium metal were studied. The polyquinone amines studied included poly-2,5-bis(1,4-phenylenediamine)-1,4-benzoquinone (pPDAQ) and poly-2,5-bis(4,4'-methylenedianilo)-1,4-benzoquinone (pMDAQ). Four simple quinoneamines 2,5-bis-4-trifluoromethylanilino-1,4-benzoquinone (TFAQ), 2,5-bis-4-methylanilino-1,4-benzoquinone (TOLUQ), 2,5-bisanilino-1,4-benzoquinone (ANILQ) and 2,5-bis-4-aminobenzoic acid-1,4-benzoquinone (PABAQ). Bandrowski's base, 2,5-diamino-1,4-benzoquinone-1,4-bis(p-phenylenediamine)imine, Figure 1, was purchased from ICN Biochemicals, and used without further purification.

Figure 1: Bandrowski's Base



## 2. EXPERIMENTAL

Melting points were obtained on a Fisher-Johns melting point apparatus, and are uncorrected. FT-IR spectra were obtained using KBr pellets on a Nicolet Magna-IR 500 Series II spectrometer using OMNIC version 3.0 software. UV-visible spectra were recorded at dilutions of 0.0500 M and  $2.00 \times 10^{-3}$  M in tetrahydrofuran (THF) or hexamethylphosphoric triamide (HMPA) on a Hewlett Packard HP 8453 UV-visible spectrophotometer using a Sigma quartz spectrophotometer cuvette. NMR spectra were obtained in deuteriochloroform using tetramethylsilane (TMS) as an internal standard on a Bruker AC-300 MHz NMR spectrometer at the Naval Research Laboratory, Washington, DC.

### 2.1 Synthesis

**2.1.1 poly-2,5-bis(4,4'-methylenedianilo)-1,4-benzoquinone (pMDAQ)** was prepared following the general procedure of Reddy, *et al.*<sup>7,8</sup> Fifteen milliliters of THF and 3.246 g of p-benzoquinone (FW = 108.10, 0.03 mol) were placed in a 4 necked 50 mL roundbottom flask, equipped with separatory funnel, condenser, and magnetic stirring bar. To this solution, 1.987 g of 4,4'-methylenedianiline (FW = 198.27 g, 0.01 mol) in 15 mL of THF was added dropwise, with stirring, over 30 minutes. Reaction progress was monitored by UV-visible spectroscopy. After five hours of reflux the reaction mixture was dark, reddish black.

The reaction mixture was allowed to cool to room temperature overnight. The dark, nearly black liquid phase was poured into a mixture of 30 mL of ice/methanol, forming an immediate red-brown turbid suspension that slowly coagulated yielding a spongy red-brown mass. This was suction filtered, and washed seven times with 25 mL of water, and 24 times with 25 mL of hot methanol. The washed solid was then dried overnight at 50 °C in a vacuum oven, yielding 2.558 g of a red-brown powder. A black solid adhering to the walls of the reaction vessel was scrapped loose, yielding 0.749 g of a flaky, gray-black solid, having a silvery surface (in contact with glass) was dried in a vacuum oven at 80 °C for 3 hours, yielding 0.695 g of dry solid. The dried solid was washed with about 50 mL of water, and five times with 25 mL of hot methanol, and dried over night in a vacuum oven at 50 °C, yielding 0.202 g of dry solid. Total yield, 2.760 g, 90%, mp >300 °C. FT/IR (mineral oil mull): 3226 N-H, 1641 C=O, 1613 C=O, 1574, 1512, 1487, 1288. Inherent viscosity: 0.183, at a concentration of 0.5 g/dL measured at 25 °C in N-methylpyrrolidinone (NMP) in a size 100 Cannon-Fenske-Ostwald viscometer. The polymer showed only partial solubility in NMP, DMSO, HMPA, morpholine, chloroform, 2-butanone, ethanolamine and methylene chloride. It was slightly soluble in acetic acid, trichloroethylene, Jeffamine D400, and ethyl acetate. It was insoluble in water, 1,1,1-trichloroethane, toluene, xylene, isopropyl alcohol and diethyl ether. The UV-visible spectrum in HMPA of the washed and dried product showed absorption maxima at 291 and 413 nm.

**2.1.2 poly-2,5-bis(*p*-phenylenediamino)-1,4-benzoquinone (PPDAQ)** was prepared similarly, by heating 3.24 g (0.03 mol) of *p*-benzoquinone in 50 mL of ethanol with 1.08 g of *p*-phenylenediamine in 50 mL of ethanol on a water bath for 3 hours, following the general procedure of Kaleem *et al.*<sup>9</sup> The resulting fine dark brown solid was filtered and washed several times with small (5 mL) portions of ethanol. The product was washed with 300 mL of water and air dried for 48 hours to yield 2.18 g of a dark brown powder. Viscosity measurements using a Cannon-Fenske size 50 viscometer and a concentration of 0.5 g/mL in THF at 22 °C, gave an inherent viscosity of 0.078, which compares favorably with literature values of 0.073 to 0.25.<sup>7</sup> FT-IR (thin film from THF, cm<sup>-1</sup>): 3230 (N-H stretch), 2958 (aryl C-H stretch), 2873 (aryl C-H stretch), 1583 (carbonyl C=O stretch), 1519 (N-H bend), 1344, 1282, 1209, 827 and UV spectra showed maxima, nm (absorbance, AU): 445.0 (1.276), 303 (1.4646) and 255 (2.0872) compare favorably to literature spectra.<sup>7,8</sup>

**2.1.3 2,5-bis-4-trifluoromethylanilino-1,4-benzoquinone (TFAQ)** In a 250 mL Erlenmeyer flask containing 50 mL of ethanol, 2.5 mL (d = 1.283 g/mL, FW = 161.13, 0.020 mol) of 4-trifluoromethylaniline was added by syringe, yielding a colorless solution. In a 100 mL beaker, 1.1017 g (FW = 108.10, 0.010 mol) of *p*-benzoquinone is dissolved in 50 mL of ethanol with stirring. The resulting yellow solution is added to the solution of 4-trifluoromethylaniline, forming a red solution. The resulting solution was allowed to stand at room temperature and open to air in a fume hood for 12 days. The resulting dark suspension was suction filtered through a Gooch crucible, yielding 1.3526 g of fine iridescent violet powder, mp > 260 °C. The resulting powder was dissolved in a mixture of approximately 150 mL of hot ethanol, 150 mL of acetic acid, and 250 mL of water. The product precipitated as a fine colloidal orange/tan solid, which was isolated by suction filtration using a Buchner funnel. FT-IR (KBr): 3432 (b, N-H), 3238 (s, N-H), 2957 (Ar-H), 2918 (Ar-H), 2850, 1733 (w, C=O), 1638 (w, C=O), 1616, 1567 (N-H), 1523, 1491, 1414, 1330, 1292, 1185, 1135, 1071, 1016, 887, 835 (*p*-disub), 771, 720, 648, 515. UV-vis  $\lambda_{\text{max}}^{\text{DMF}}$  nm (log  $\epsilon$ ): 278 (4.35), 364sh (4.31), 378 (4.30), 490sh (2.84). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  1.25, s, 2 H (2 N-H);  $\delta$  7.38, d, J = 8.7 Hz, 4H, (2 *p*-disubstituted aromatic adjacent to amine);  $\delta$  7.69, d, J = 8.7 Hz, 4H, (2 *p*-disubstituted aromatic adjacent to trifluoromethyl);  $\delta$  8.11, s, 2H, (quinone enone, adjacent to N).

**2.1.4 Other simple quinone amines** were prepared analogously:

- 2,5-bis-4-aminobenzoic acid-1,4-benzoquinone (PABAQ): red powder, mp >260 °C, 29.9% yield. FT-IR (KBr): 3600-2400 (b, COOH), 3271 (NH), 2981 (Ar-H), 2669, 2550, 1683 (s, C=O), 1649, 1616, 1584 (N-H), 1521, 1420, 1289. 1234, 1173, 1126, 900, 846 (*p*-disub), 798, 770, 719, 547, 522, 413.

- 2,5-bis-4-methylanilino-1,4-benzoquinone: brown powder, mp >260 °C, 19.8% yield. FT-IR (KBr): 3240 (s, N-H), 1635 (w, C=O), 1559 (N-H), 1516, 1481, 1410, 1354, 1287 (N-H), 1234, 1190, 866, 829, 779, 778, 727, 571, 486, 452.

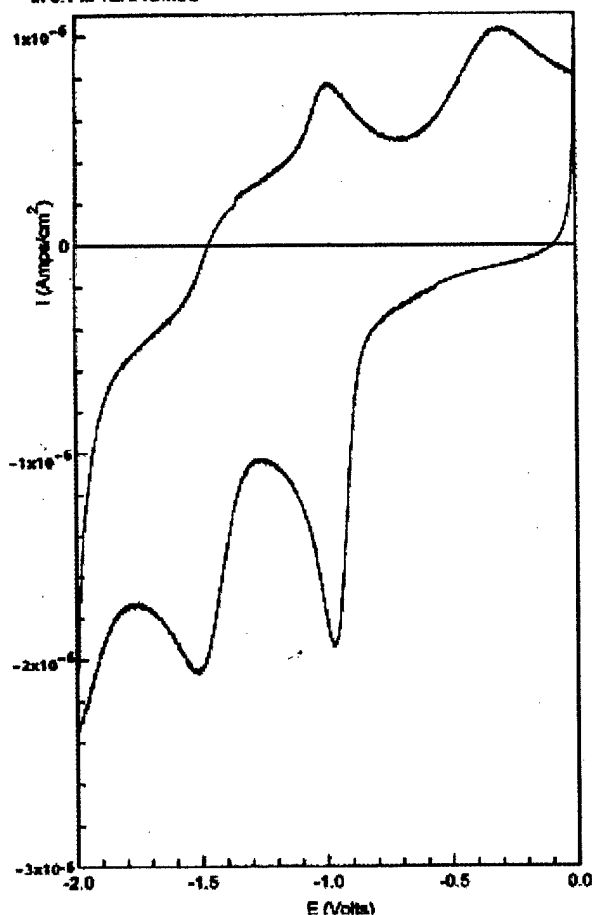
- 2,5-bisanilino-1,4-benzoquinone: violet powder, 31% yield. FT-IR (KBr): 3236 (s, N-H), 2918 (w, Ar-H), 1733 (w), 1638 (w, C=O), 1568 (N-H), 1504, 1491, 1444, 1357, 1288 (N-H), 1188, 895, 841, 743 (monosubs), 726, 694 (monosubs), 495.

**2.3 Cyclic voltammetry** Cyclic voltammograms were recorded using an EG&G Princeton Applied Research (PARC) Potentiostat/Galvinostat Model 273A and Schlumberger (Solartron) SI 1255 High Frequency Response Analyzer (FRA), using Scribner Associates, Inc. CorrWare for Windows electrochemistry/corrosion software and CorrView graphing software. The working electrode was a 2 mm diameter glassy carbon millielectrode, and reference electrodes were silver/0.01 M silver nitrate/acetonitrile, silver/0.1 M silver nitrate/dimethylsulfoxide (DMSO) or silver/0.1 M silver nitrate/*N,N*-dimethylformamide (DMF), depending upon the solvent used for the experiment. The electrolyte was 0.1 M tetra-*n*-butylammonium perchlorate (TBAP) in the appropriate polar aprotic solvent. A ferrocene standard in acetonitrile was run before experimental trials, and solvent blanks were obtained immediately prior to each experiment. DMF and DMSO from freshly opened bottles were dried over 0.3 nm (3 Angstrom) molecular sieves and stored under nitrogen. A 0.020 M stock solution was prepared by diluting the weighed sample. The resulting turbid suspension was then heated in an oil bath at 100 °C for an hour to aid in dissolution. Then, 500 µL of the stock solution was transferred to 10 mL of the 0.1 M electrolyte blank solution using a Drummond digital microdispenser. Additional 500 µL - 1 mL aliquots were added to observe signal intensity changes.

*p*-Benzoquinone in 0.1 M TBAP in acetonitrile gave a cyclic voltammogram matching the literature voltammogram,<sup>13</sup> having a first reduction peak near -0.6 V (formation of the radical anion) and a second reduction peak, near -1.6 V (formation of the dianion).

**2.3.1 Simple Quinone amines** Neither the simple quinone amines or quinone/amine polymers are soluble in acetonitrile. In DMSO, TFAQ showed two reductions, at about -0.9 V and -1.5 V versus silver/silver nitrate electrode, shown in Figure 2. By analogy to benzoquinone, these correspond to formation of the radical anion and dianion, respectively. Electron donation through conjugation by the amine lone-pair has shifted the first reduction to more negative potential, by about -0.3V. The reverse scan shows two oxidation peaks, around -1.0 V and -0.3V, with a plateau around -1.3V. It is likely that the plateau around -1.3V represents oxidation of the dianion, and the peak around -1.0 V represents oxidation of the radical anion to the quinone. The third oxidation, around -0.3 V could represent oxidation of the arylamine to an imine. The distortion and lack of symmetry of these oxidation peaks suggests a physical process – such as adsorption to the electrode, or a chemical reaction – such as disproportionation or protonation of an anion - has occurred following reduction.

Figure 2. Cyclic voltammogram of 10 microMolar TFAQ in 0.1 M TBAP/DMSO

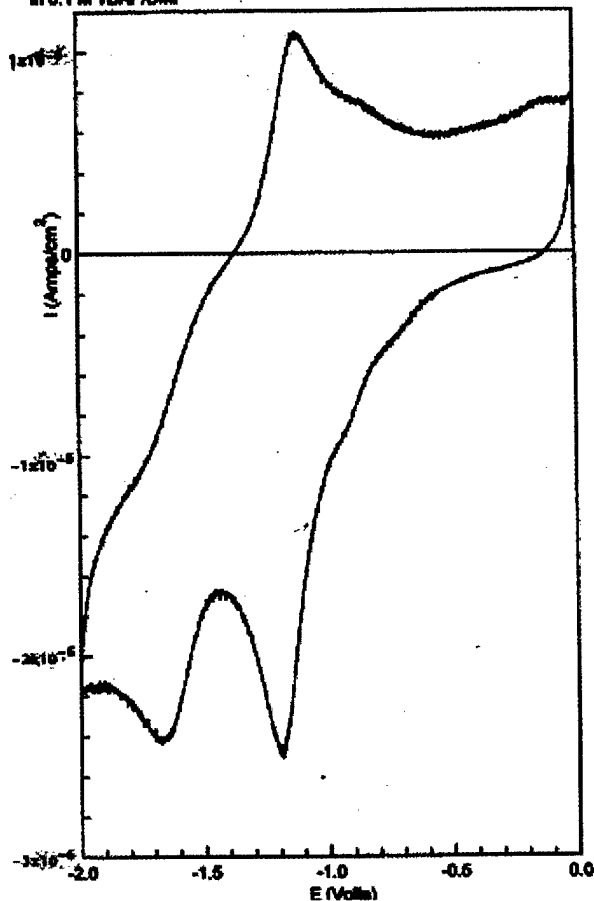


Other simple quinoneamines gave similar cyclic voltammograms. PABAQ in DMF showed a reduction at -0.7 V, most likely the carboxylic acid forming a carboxylate anion. A second reduction at -1.0V corresponds to the formation of the quinone radical anion. The reverse scan showed a shoulder around -0.7 V (oxidation of the radical anion) and an oxidation peak near -0.5 V, (oxidation of the carboxylate anion). A third, unidentified oxidation occurred around -0.25 V. Lack of symmetry of the reverse scan is characteristic of a physical process or a chemical reaction. ANILQ shows two reductions in DMF. The first reduction, at -0.95 V (formation of the radical anion), and the second, at about -1.5 V (formation of the dianion). On the reverse scan, a shoulder near -1.25 V (oxidation of the dianion to the radical anion,) and an oxidation near -0.7 V (oxidation of the radical anion to the quinone.) These oxidations again showed distortion indicating physical processes or chemical reaction.

**2.3.2 polyquinoneamines** pPDAQ was only partially soluble in hot DMF. It showed reduction to the radical anion at -1.2 V, and to the dianion at -1.7 V (Figure 3). On the reverse scan, a shoulder near -1.5 V represents oxidation of the dianion to the radical anion. The oxidation peak at -1.1 V represents oxidation of the radical anion to the

quinone. Lack of symmetry of both peaks suggests physical processes or chemical reaction.

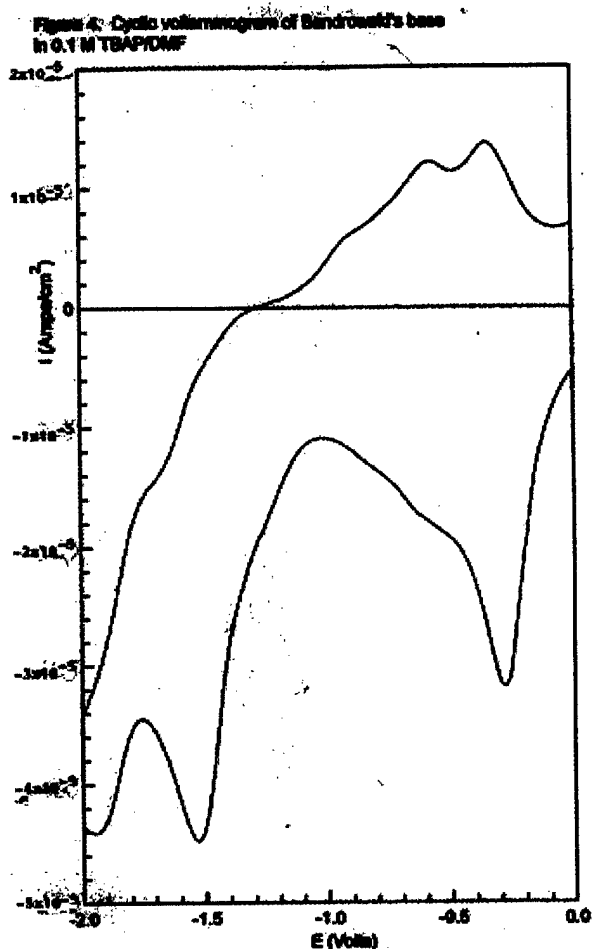
Figure 3. Cyclic voltammogram of 20 micromolar pPDAQ in 0.1 M TBAP/DMF



pMDAQ is only slightly soluble in DMF, where it shows a reduction around -1.0V. The voltammogram is broad and featureless, with the hint of a second reduction around -1.4 V. By analogy to p-benzoquinone and TFAQ, these correspond to formation of the radical anion and dianion, respectively. The reverse scan is also broad, with an oxidation near -1.0 V, with the hint of other oxidations around -0.6 and -0.4 V in DMF. These likely correspond to oxidation of the radical anion, and to amine oxidations, respectively. The broad, featureless structure and lack of symmetry in the forward and reverse scans again suggest the presence of physical and/or chemical processes.

**2.3.3 Bandrowski's base** (Figure 4) shows reduction to a radical anion at -0.282 V, with a shoulder at -0.598V. Reduction to a dianion occurs at -1.52V, with a third reduction at -1.94 V in DMF. The reverse scan again shows broad features characteristic of physical and/or chemical processes. These include shoulders at -1.71V, -1.25 V and -0.84V, and oxidation peaks at -0.574 and -0.346 V.





**2.4 L-10 Solubility/Compatibility Testing** AroCy L-10 cyanate ester (ethylidene bis-4,1-phenylene dicyanate, Ciba Specialty Chemicals) was used as a model for galvanically induced degradation. Approximately 1% solutions of Bandrowski's base, TFAQ, and pMDAQ in L-10 were prepared by adding about 10 mg samples of the appropriate quinone/amine to roughly 1 g of L-10 monomer, with stirring and heating to 80-90 °C for one hour. Where undissolved solids remained, and the resulting solutions were turbid, additional L-10 polymer was added forming 0.5% solutions, which were heated with stirring for an hour.

**2.5 Differential Scanning Calorimetry** (DSC) was performed on an L-10 blank and the 0.25% quinone/amine L-10 solutions using a TA Instruments 2920 DSC equipped with a 3100 controller. Samples were heated from room temperature to 300 °C at 3 °C/min, modulated at 60 cycles for curing. They were allowed to cool back to room temperature, and then returned to 300 °C at the same rate. No additional exotherms were observed during the second heating, indicating complete curing during the first heating cycle. The quinone/amines were compatible with L-10 monomer based on DSC results. Exotherm (polymerization) onset was at 154 °C, reaching a maximum at 213 °C for the L-10 blank. Onset and maxima were 170 °C and 214 °C for Bandrowski's base, 160 °C

and 214 °C for TFAQ, and 187 °C and 245 °C for pMDAQ, which showed a second exotherm near 250 °C.

**2.6 Layup** Corrosion test coupons were cut from 316 cm<sup>2</sup>, 9 ply panels. Two blank test panels were prepared from 3413 cm<sup>2</sup> Magnamite prepreg AS-4 graphite fiber (Hercules Aerospace Division). The carbon fiber was placed on 1.4 x 1.9 m Wrightlon 8400 blue 0.0762 mm nylon bagging film, and treated with 79.4 g L-10 resin at 60 °C. L-10 resin containing 0.25% quinone/amines (0.199 g) were heated for 1 hour at 90 °C with stirring and poured on sample carbon fibers (pPDAQ was practically insoluble in L-10 resin). Bagging was folded over the carbon fiber, and the resin spread evenly to wet the entire surface. The bagging containing the fiber was flipped over, and spreading was continued on the opposite surface. Bagging and fiber were trimmed to remove the outer inch, marked, and trimmed into nine 316 cm<sup>2</sup> squares. These were stacked, alternately flipped and rotated 90°. Two additional 929 cm<sup>2</sup> panels – one containing only AroCy L-10 as a blank, the other containing 1% Bandrowski's base – were similarly prepared. Nine ply BMI panels – both blank and containing 2% Bandrowski's base – were prepared using Ciba Geigy Matrimid 5292 A + B (100/85).

The blank and sample panels were cured in a General Signal Company Blue M Electric walk-in vacuum oven. Aerospace Service & Controls Composite Processing Control (CPC) software was used to ramp the temperature for CE panels at a rate of 10°/minute to 150 °C for 2 hours, 200 °C for 1 hour, and 300 °C for one hour. Final test panel thickness was 1.8 mm, with resin content ranging from 28 to 29 per cent. The two BMI components were combined and heated with continuous stirring to 120 °C. Panels were cured for 1 hour at 180 °C, 2 hours at 200 °C, and 6 hours at 250 °C.

**2.7 Corrosion Testing** Coupons for corrosion tests were cut from the 9 ply panels. The 7.6 x 2.5-cm coupons were attached to 5.0 x 2.5-cm aluminum using titanium bolts, which were tightened to 0.23 kg m using a torque wrench. The solution/air interface was at the middle of the coupon, roughly bisecting the titanium bolt. Initial screening involved placing coupons in plastic containers with 3.5% aqueous sodium chloride in a laboratory oven at 82 °C for 68 hours. A second series of corrosion tests were performed at room temperature with coupons placed in separate loosely covered glass jars.

After 68 hours at 82 °C, most CE coupons showed significant polymer leaching above the air/water interface, leaving an easily bendable graphite skeleton. Only the sample containing 1% Bandrowski's base remained essentially intact.

BMI coupons required much longer time for degradation than cyanate esters. Within a week significant amounts of polymer had leached out of the test coupon over the aluminum. Some polymer also sublimed on a watch glass that was placed loosely over the sample jar. The aqueous phase became frothy and light brown. Definite swelling was observed within 9 days. By the 11<sup>th</sup> day samples containing 2% Bandrowski's base were becoming flexible, while the blanks remained rigid. Within two samples containing 2% Bandrowski's base showed extensive swelling and delamination. At the end of three weeks, samples containing Bandrowski's base showed extensive degradation, while only one of the blanks exhibited swelling.

**2.7.1 pH measurements** were recorded using an Orion Research digital ionalyzer model 501 equipped with Corning general purpose combination electrodes. A Corning pH30 and dual tint pH paper were also used for pH measurements.

**2.7.1.1 Cyanate esters.** Samples containing 1% Bandrowski's Base and blank test coupons at room temperature in 3% aqueous sodium chloride showed evidence of reaction within 48 hours. A white aluminum oxide and bubbles form along the edges of the aluminum submerged in water, from the titanium bolt downwards, and at the water line. Initially samples containing Bandrowski's base produced solutions that are more acidic (0.22-0.4 pH unit, roughly twice as acidic) than the blank. Increasing acidity is likely due to increased  $\text{Al}^{3+}_{(\text{aq})}$  – suggesting that samples containing Bandrowski's base initially corrode more rapidly than the blank.

Within three days bubbles are visible around the aluminum/cyanate ester interface below the water line. A white colloidal suspension of aluminum hydroxide was visible from the titanium bolt downward. Black material, most likely degraded polymer, is visible on top of the aluminum. Solution acidity increased for both the sample and the blank, but uncertainty also increased as shown by increased standard deviation.

Within a week, the pH of the sodium chloride solution decreased from about 7 to around 6. More bubbles are observed at the air/water interface and along the aluminum/composite interface below the water, and along the titanium nut below the water. Increasing cloudiness is observed in the water, from titanium bolt downward and at the bottom of the container.

A reddish/white solid gel and clear liquid appears along the aluminum above the water line, having a basic pH of 8.8 in the region of degradation, indicating an aqueous hydroxide solution. The white solid is possibly a deliquescent aluminum hydroxide. The red color is due to polymer degradation.

At the end of two weeks, much more white solid is observed around the edge of the aluminum above the water and bubbles appear at the surface. There is a 1-2 cm white dense cloudy layer at the bottom and below the water along the edge of the aluminum. Water droplets along the aluminum/composite/air interface have a pH=9.4, using pH paper. A general trend – all samples are becoming more acidic. Blanks are becoming more acidic than those containing Bandrowski's base.

By the third week, the aqueous solution in samples containing Bandrowski's base remains virtually unchanged (pH 6.20 – 6.28) while the blank has decreased to pH 4.19 – 5.92. This suggests that less aluminum ion is produced by the samples containing Bandrowski's base. After three weeks there is more hygroscopic material over the aluminum, and some pitting of the surface of the composite. A reddish coating on the aluminum is visible on the unsealed blank. The pH on the upper surface of the aluminum is 9.4.

2.7.1.2 *BMI* test coupons exhibited bubbles on the bottom and sides of the aluminum within 5 hours. A faint white turbidity, from the edges of the aluminum to the bottom of the sample jar was observed within a day. A dark grey coating was observed on the aluminum. By the second day white gelatinous material was observed from the edges of the aluminum to the bottom of the flask. Large bubbles, roughly 0.5 cm diameter, formed along the aluminum edge. A red material was observed on the aluminum beneath the water line. By the third week, a general trend was observed. The aqueous layer from both blanks and samples containing 2% Bandrowski's base were becoming basic. Samples containing 2% Bandrowski's base were less basic than the blanks.

### 3. DISCUSSION

Reactions occur at several interfaces in coupons undergoing corrosion. The aluminum/titanium, air/water interface is the site of initial reaction. Below the titanium bolt an insoluble acidic aluminum oxide gel forms and spreads downward over the aluminum surface forming a white colloidal suspension at the bottom of the glass reaction jar. Bubbles of hydrogen form below the titanium bolt, and along the aluminum/composite interface in the aqueous salt-water solution. A deliquescent, white, basic aluminum oxide forms above the titanium bolt at the titanium/aluminum-air interface and along the aluminum/composite-air interface.

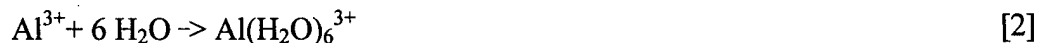
Chloride ion acts as a Lewis base, weakening the aluminum oxide coating on the aluminum. Exposed aluminum is oxidized by oxygen in the air forming aluminum cation and electrons. Aluminum ions enter the aqueous layer, forming hexaaquoaluminum (III) ( $\text{Al}(\text{H}_2\text{O})_6^{3+}$ ), an acidic cation.

Reactions include:

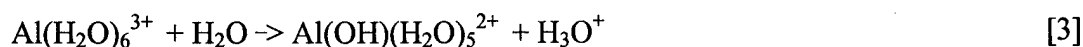
- oxidation of aluminum:



- hydration of aluminum ion:



- and protonation of water, forming the acidic solution:



Some of the electrons released by the aluminum travel through the graphite of the composite to the aqueous layer, where they react with hydronium ions forming hydrogen. Other electrons travel through the graphite of the composite to react with oxygen in the air, forming superoxide radical anion, initially. Superoxide reacts with water to form hydroperoxy radical and hydroxide ion. The hydroxide ion likely complexes with aluminum oxide to form tetrahydroxyaluminate (III) ( $\text{Al}(\text{OH})_4^-$ ). The hygroscopic white solid is likely aluminum tetrahydroxyaluminate (III) ( $\text{Al}(\text{Al}(\text{OH})_4)_3$ ). This species is the likely catalyst for polymer degradation. The aluminum cation could act as a Lewis acid catalyst, while the tetrahydroxyaluminate (III) anion would provide the nucleophilic hydroxide ion.

BMI degradation releases 4,4'-methylenedianiline, a base. This base neutralizes hydronium ion formed by aqueous aluminum. Excess 4,4'-methylenedianiline reacts with water, forming hydroxide ion, leaving the aqueous layer in BMI samples basic.

#### 4. CONCLUSION

Bandrowski's base offers limited corrosion protection in aqueous sodium chloride solution for composites prepared from L-10 cyanate ester. However it appears to cause increased degradation in BMI. Bandrowski's Base may be ineffectively incorporated into the composite structure due to interference with reactions during BMI curing. These reactions include the "ene"-reaction and Diels-Alder reaction. Allyl groups undergo both Diels-Alder and "ene"-reactions. Modifying Bandrowski's base by N-allylation with allyl halide or tosylate would allow the quinone imine to be more effectively incorporated into the cured BMI composite. This work is currently underway.

#### 5. SUMMARY

Various quinone/amines were evaluated as potential redox inhibitors of bismaleimide (BMI) degradation, using Arocy-L10 cyanate ester/graphite as a model for BMI-based composites. Cyclic voltammetry was performed to assess the ability of quinone/amines as electron acceptors in nonpolar aprotic solvents. Corrosion tests were performed on coupons made from graphite reinforced cyanate resin treated with quinone/amines, and with BMI. Bandrowski's base - a quinone/amine imine - proved to be the most promising candidate for producing corrosion resistance in cyanate ester. However, it appeared to catalyze degradation in commercial BMI resin systems.

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